

IV.H.11 CO Sensors for Fuel Cell Applications

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Objectives

- Develop an intermediate temperature reformat pre-stack CO sensor to detect 1-100 ppm CO at < 150°C with a response time of 0.1-1 sec and an uncertainty of 1%-10%.
- Develop a high temperature CO sensor to detect 100-1000 ppm CO at ~ 250°C with a response time of 0.1-1 sec and an uncertainty of 1%-10%.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- B. Sensors

Approach

Two electrochemical sensor types are being investigated for high and low temperature carbon monoxide sensing:

- An amperometric device based on the carbon monoxide inhibition of hydrogen oxidation kinetics at the electrodes of a PEM fuel cell is being developed for the low temperature application.
 - Sensors based on perfluorosulfonic acid polymer electrolytes are being evaluated.
 - Different catalyst loadings of carbon supported and un-supported Pt, Ru and Pt/Ru alloys are being evaluated as electrodes.
- An solid oxide electrolyte device based on the kinetics of the electrode reactions is being developed for both the high and low temperature application.
 - Yttria-doped zirconia and gadolinia-doped ceria oxygen ion conductors are being investigated as the solid electrolyte.
 - Several metals including Pt, Pd, Au, Ru and Ni are being evaluated as the sensing and reference electrodes.

Accomplishments

- Low temperature electrochemical sensors have been developed to sense CO concentrations between 10-1000 ppm in a reformat stream.
- The detection range and response time of the CO sensors can be tuned by adjusting the precious metal loading of the sensing electrode.

- The intermediate temperature polymer-based sensors have been successfully tested in the effluent stream of a preferential oxidation reactor and have a response comparable to that of analytical non-dispersive infrared analyzers.
- A heater has been incorporated in the previously developed oxide based high temperature (150-250°C) sensors.

Future Directions

- Evaluate the effect of sulfur and ammonia on the sensor response.
- Improve the response time of the sensors using signal processing techniques.
- Identify industrial partner to transfer technology.

Introduction

The detection and measurement of carbon monoxide in high temperature reformat streams is of vital importance to the successful implementation of fuel cells for transportation. Much research is being performed to optimize low cost fuel reformer systems that convert liquid hydrocarbon fuels to hydrogen gas-containing fuel streams. This hydrogen gas typically feeds a polymer electrolyte membrane (PEM) fuel cell utilizing a platinum-based anode. It is well known that low concentrations (10-100 ppm) of carbon monoxide impurities in hydrogen can severely degrade the performance of PEM fuel cell anodes.¹ This performance degradation is due to strong adsorption of carbon monoxide on the electro-active platinum surface sites where hydrogen is normally oxidized to protons.¹

Therefore, the proper design of combined fuel cell stack and reformer systems must pay careful attention to the minimization of carbon monoxide before the processed fuel stream enters the stack. Many reformer systems use a secondary preferential oxidation (PrOx) reactor that selectively oxidizes the carbon monoxide present in the reformat stream. The efficiency of this PrOx reactor will depend on the accurate and rapid measurement of the inlet (or outlet) CO concentration at the reactor. Moreover, current fuel cells use air-bleeding methods to reduce the carbon monoxide poisoning of the Pt anode. Since this method involves the mixing of 2-6% air with the fuel stream, it results in a decrease in the energy efficiency of the fuel cell system and can greatly benefit from the accurate determination of the

CO content of the fuel stream entering the stack. Hence, CO sensors that measure the CO content of the fuel stream before and after the PrOx reactor can be used for feedback control, thus allowing these integrated fuel cell systems to operate at maximum energy efficiency. Solid-state electrochemical sensors meeting these criteria, including the demonstration of prototype sensors, are being designed and developed.

Approach

Low temperature carbon monoxide sensors

Los Alamos National Laboratory (LANL) is developing intermediate temperature carbon monoxide sensors based on the reversible carbon monoxide adsorptive poisoning of precious metal electrodes. The addition of metals such as ruthenium to the platinum anode catalyst is known to greatly improve the hydrogen-oxidation kinetics in the presence of CO. An amperometric sensor that senses the differential CO inhibition of the hydrogen oxidation reaction at 2 electrodes can be fabricated from a platinum electrode, a proton conductor and a platinum ruthenium alloy electrode. While the current density of the platinum electrode will be influenced by the surface coverage of carbon monoxide, the current density at the Pt/Ru alloy electrode should be relatively unaffected. In this project the electrode composition, precious metal loading and operating temperature of these amperometric sensors are optimized in order to develop a CO sensor that will sense 1-100 ppm CO in the inlet fuel stream of a fuel cell stack.

High temperature carbon monoxide sensors

High temperature zirconia and ceria-based electrochemical sensors to measure CO in hydrogen streams are also being developed at LANL. These sensors would operate at 150-400°C and can be used for feedback control either before or after the PrOx reactor. We have successfully developed novel mixed-potential sensors that are capable of measuring ppm levels of CO in air. The unique design of these sensors makes them robust, stable and reproducible.² In this project we are working on modifying the electrodes of these devices to enable them to work in a hydrogen atmosphere.

Results

Low temperature carbon monoxide sensors

The PEM based sensors are amperometric sensors that use adsorption of CO on the working electrode to reduce the current flow at a given potential. In previous years we demonstrated a CO sensor working at room temperature that was sensitive to 0-100 ppm CO. However when the operating temperature was raised to 70-80°C, the sensitivity greatly decreased (100-1000 ppm). In this fiscal year we were able to optimize these sensors in order to successfully meet the DOE requirements (except response time at low CO concentrations) for a pre-stack CO sensor.

The sensors were made of Nafion 117 electrolyte and Pt/Ru (50/50 alloy)/Nafion pseudo reference electrodes with a precious metal loading of 10 mg/cm². The working electrode was either Pt/C/Nafion at a Pt loading of 0.2 mg/cm² or Pt/Nafion at a Pt loading of 10 mg/cm². The sensors (Figure 1) were approximately 0.25 cm² in area and were sandwiched between double-sided carbon/teflon gas diffusion layers (E-Tek). The sensors were inserted in the exhaust stream of a PrOx reactor where the total flow rate was approximately 125 L/min and the gas consisted of 0-2000 ppm CO in a 40% H₂, 25% N₂, 17.5% CO₂, 17.5% H₂O stream. A non-dispersive infrared (NDIR) CO analyzer (California Analytical Instruments) was used to measure the actual CO content of the gas downstream of the sensor.

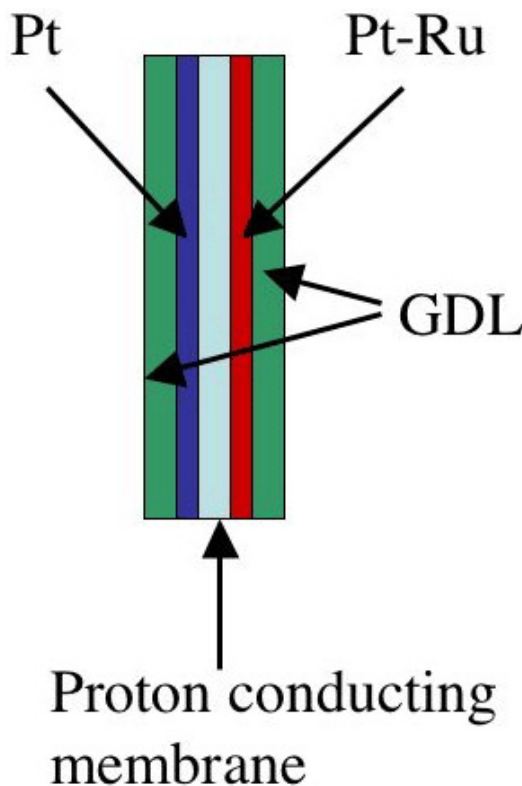


Figure 1. Schematic of a low temperature Nafion based sensor. GDL = Gas diffusion layer (E-TEK), Pt-Ru = 10 mg/cm² of Pt/Ru (50/50 alloy)/Nafion. Pt = either 0.2 mg/cm² of Pt/C/Nafion or 10 mg/cm² of Pt/Nafion. Proton conducting membrane = Nafion 117.

The response to 0 - 100 ppm CO of a PEM sensor with a catalyst loading of 0.2 mg/cm² is shown in Figure 2 along with the response of the NDIR CO analyzer. This sensor is very sensitive to low concentrations of CO where the sensor current at 0.3V decreased by 64% when the CO content increased from 0 to 100 ppm. Moreover, the response time of the sensor decreased with increasing concentrations of CO and was greater than a few minutes when the CO concentration was < 25 ppm and was 1 sec when the CO concentration was 75-100 ppm. The response of this sensor and that of the CO analyzer to cycling CO concentration between 50-150 ppm is shown in Figure 3. It is seen that the performance of this sensor is comparable to the response of the CO analyzer under these test conditions. This sensor meets all the DOE requirements except for the response time, which is

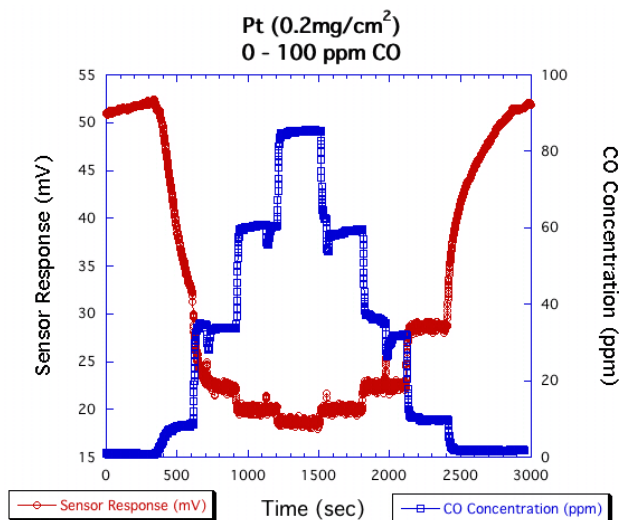


Figure 2. Response of PEM sensor with a 0.2 mg/cm² Pt/C/Nafion working electrode to 25, 50, 75, and 100 ppm CO at T = 85°C and V = 0.3 V. The response of a NDIR CO analyzer is also shown for comparison.

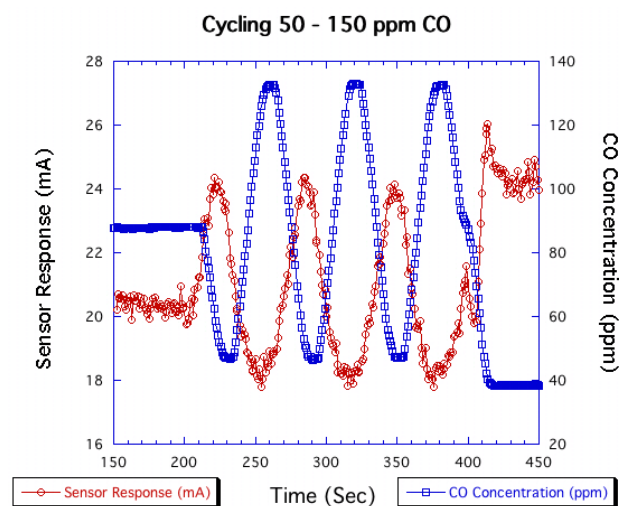


Figure 3. Response of PEM sensor with a 0.2 mg/cm² Pt/C/Nafion working electrode to cycling CO between 50 ppm and 150 ppm at T = 85°C and V = 0.3 V. The response of a NDIR CO analyzer is also shown for comparison.

greater than DOE's prescribed 1 sec when the CO concentration drops below 75 ppm. However, this may not be a critical factor since the next generation of fuel cells is expected to be tolerant to low (< 50 ppm) levels of CO and the sensor response time

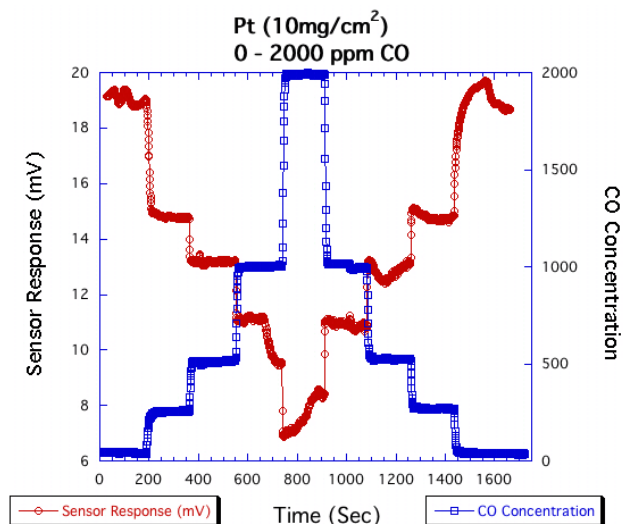


Figure 4. Response of PEM sensor with a 10 mg/cm² Pt/Nafion working electrode to 250, 500, 1000, and 2000 ppm CO at T = 80°C and V = 0.1 V. The response of a NDIR CO analyzer is also shown for comparison.

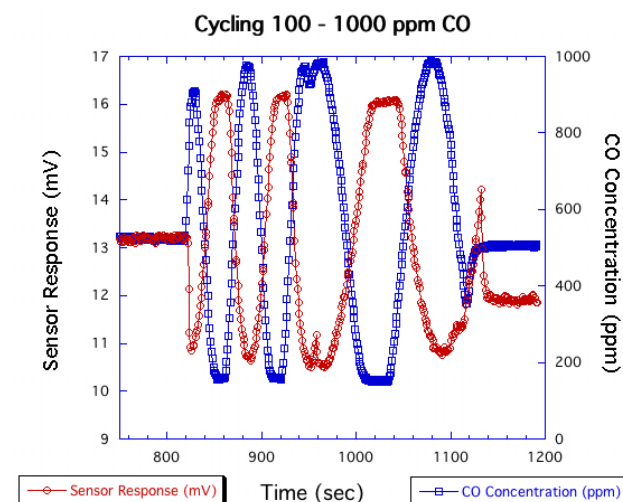


Figure 5. Response of PEM sensor with 10 mg/cm² Pt/Nafion working electrode to cycling CO between 100 ppm and 1000 ppm at T = 80°C and V = 0.1 V. The response of a NDIR CO analyzer is also shown for comparison.

improves to < 1 sec when the CO concentration is >75 ppm.

The response from the sensor with high catalyst loading (10 mg/cm²) is presented in Figures 4 and 5. The response current at 0.1 V decreased by 68% as the

CO content increased from 0 to 2000 ppm. For this sensor, increasing the precious metal loading of the working electrode resulted in an increase in the sensor saturation limit and a decrease in the sensor sensitivity and response time. The response time of this sensor was comparable to that of the infrared analyzer at low CO concentration, while at high CO concentrations the sensor response times were significantly better than that of the analyzer. The response times of this sensor is sufficient to follow CO cycles between 100-1000 ppm with periods > 30 seconds. Therefore this sensor has the potential to monitor the inlet CO concentration to the PrOx reactor.

High temperature carbon monoxide sensors

In the previous year we had developed high temperature CO sensors based on ceria and zirconia electrolytes. A sensor with a $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (CGO) electrolyte and Ni and Pt electrodes had a response of 40 mV to 500 ppm of CO at 250°C. This sensor has the potential to monitor the input CO concentration to a PrOx reactor if its response time and stability could be improved. However, this sensor was externally heated using a furnace and could not be tested under practical conditions. During this fiscal year we designed a Pt heater (mask shown in Figure 6) that could be incorporated on the sensor body. Using standard photolithography and electron beam evaporation techniques we were able to successfully deposit a Pt strip heater on the CGO substrate of the sensor. The power requirement for this sensor was <5 watts with this heater design.

Conclusions

- Low temperature pre-stack CO sensors based on Nafion membranes have been developed.
- The response time and sensitivity of these sensors can be tuned by adjusting the precious metal loading of the working electrode.
- A sensor with a Pt working electrode (0.2 mg/cm^2) meets all the requirements (except response time) listed by the DOE for a pre-stack CO sensor.



Figure 6. Mask of Heater Assembly for the High Temperature Sensors

- The response time of these sensors is slow (several minutes) at low (<25 ppm) concentrations of CO and improves to <1 sec at high (>75 ppm) concentrations of CO.
- A heater has been incorporated into the high temperature oxide-based CO sensors reducing their power requirements to less than 5 watts.

References

1. S. Gottesfeld and T. Zawodzinski in *Advances in Electrochemical Science and Engineering*, **5**, pp. 219-225 (1998).
2. Rangachary Mukundan, Eric. L. Brosa and Fernando H. Garzon, Electrodes for Solid State Gas Sensors, U.S. Patent 6,605,202, August 12, (2003).

FY 2004 Publications/Presentations

1. R. Mukundan, E. L. Brosha, and F. H. Garzon, An Electrochemical Sensor For The Detection Of Carbon Monoxide In Hydrogen-Containing Streams. Presented at the 204th Meeting of the Electrochemical Society, Florida, October 12-17 (2003).
2. R. Mukundan, E. L. Brosha, and F. H. Garzon, A low temperature sensor for the detection of carbon monoxide in hydrogen. Accepted for publication in a special issue of the Journal of *Solid State Ionics*.
3. R. Mukundan, Eric L. Brosha, Michael A. Inbody and Fernando H. Garzon. Carbon Monoxide Sensors for Application in Polymer Electrolyte Membrane Fuel Cells. Accepted for publication in the Proceedings of Chemical Sensors VI, The Electrochemical Society Inc. (2004).